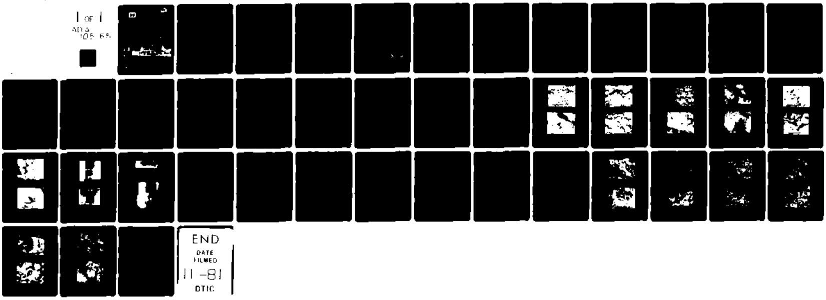
AD-A105 165 ARMY ENGINEER WATERWAYS EXPERIMENT STATION VICKSBURG--ETC F/6 11/2
EXAMINATION OF ERDA-10 GROUT SPECIMENS AT DIFFERENT AGES.(U)
AUG 81 A D BUCK, J P BURKES, J E RHODERICK DE-AI97-81ET46633
UNCLASSIFIED WEP/MP/SL-81-20 NL



LEVEL II

AD A105165

MISCELLANEOUS PAPER SL-81-20

EXAMINATION OF ERDA-10 GROUT SPECIMENS AT DIFFERENT AGES

by

Alan D. Buck, Jerry P. Burkes, Jay E. Rhoderick

Structures Laboratory
U. S. Army Engineer Waterways Experiment Station
P. O. Box 631, Vicksburg, Miss. 39180

August 1981

Final Report

Approved For Public Release; Distribution Unlimited

Prepared for Sandia National Laboratories
Albuquerque, N. Mex. 87115
and
Office of Nuclear Waste Isolation
Battelle Memorial Institute
Columbus, Ohio 43201

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: Miscellaneous Paper SL-81-20

2. GOVT ACCESSION NO.: AD-A105 165

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle): EXAMINATION OF ERDA-10 GROUT SPECIMENS AT DIFFERENT AGES

5. TYPE OF REPORT & PERIOD COVERED: Final report

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s):
Alan D. Buck
Jerry P. Burkes
Jay E. Rhoderick

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
U. S. Army Engineer Waterways Experiment Station
Structures Laboratory
P. O. Box 631, Vicksburg, Miss. 39180

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

11. CONTROLLING OFFICE NAME AND ADDRESS:
Sandia National Laboratories
Albuquerque, N. Mex. 87115 and
Office of Nuclear Waste Isolation
Battelle Memorial Institute, Columbus, Ohio 43201

12. REPORT DATE: August 1981

13. NUMBER OF PAGES: 38

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

15. SECURITY CLASS. (of this report): Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

Available from National Technical Information Service, 5285 Port Royal Road, Springfield, Va. 22151.

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Borehole plugging
Cement grout
Grout
Petrographic examination
Scanning electron microscope
X-ray diffraction

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

A borehole designated ERDA-10 was filled with portland cement based grout in October 1977. The borehole is located in Eddy Co., N. Mex. The hole was filled with grout of four compositions, three of which were similar and made with salt water as mixing water; the upper portion of the hole was filled with a grout made using fresh water as mixing water. During the filling operation, test specimens were cast using these grouts. The deepest plug (plug 1) was cored 48 hours after placement. During the filling operation, test specimens

(Continued)

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

20. ABSTRACT (Continued)

were cast using all four grout compositions. The core from plug 1 and the test specimens were sent to the Structures Laboratory of the U. S. Army Engineer Waterways Experiment Station for physical tests and petrographic examination. They were stored in the laboratory at temperatures ranging from about 23°C to 54°C.

Tests and examinations were made at three ages: (a) 23 ± 8 days, (b) approximately 1 year, and (c) approximately 3 years. This report presents the results of the petrographic examination which included use of X-ray diffraction (XRD) and scanning electron microscopy (SEM).

The grouts made with salt water formed tetracalcium aluminate dichloride-10-hydrate ($C_3A(CaCl_2)H_{10}$) at the expense of ettringite during continued hydration. The $C_3A(CaCl_2)H_{10}$ was already present when the grouts were examined at the early ages (23 ± 8 days).

The amount of calcium hydroxide in both the saltwater and the freshwater grouts decreased with age. The calcium hydroxide presumably was reacting with the fly ash in the grout to produce calcium silicate hydrate.

The microstructures of the grouts showed progressive densification with age. This microstructure was always fairly open due to the high water-to-solids ratios; these were 0.64 to 0.74 by mass for the three saltwater grouts and 0.49 for the freshwater grouts.

Phase composition and microstructure were considered normal for these materials; the range of temperature from about 23°C up to about 54°C did not seem to have any detectable effect on composition or microstructure.

It was found that carbonation had taken place during 3 years of immersion in salt water or fresh water. Carbonation was largely confined to surfaces of specimens.

Some cracking of specimens had taken place. This is ascribed to a combination of several factors which included shrinkage after heat of hydration expansion, possible short periods of drying during storage and during intermittent testing, and possible expansion due to continued hydration after the initial cooling.

In spite of some carbonation and cracking of specimens, the earlier published and present data suggest that these grouts should be regarded as satisfactory compositions for their intended purpose.

PREFACE

The work described in this report was funded by the U. S. Department of Energy. It was begun in connection with studies conducted in cooperation with Sandia National Laboratories. It was completed under U. S. Department of Energy Interagency Agreement DE-AI97-81ET46633, subject, "Investigation of Composition and Properties of Cementitious Mixture for Boreholes and Shafts."

Mr. Floyd L. Burns of the Battelle Office of Nuclear Waste Isolation in Columbus, Ohio, was Project Manager for the work starting in 1980.

The work was done in the Structures Laboratory (SL) of the U. S. Army Engineer Waterways Experiment Station (WES) under the general supervision of Mr. Bryant Mather, Laboratory Chief, and Mr. John M. Scanlon, Jr., Chief, Concrete Technology Division. Messrs. John A. Boa, Jr., and Donald M. Wally were co-Project Leaders. This report was prepared by Mr. Alan D. Buck from data prepared by Messrs. Jay E. Rhoderick and Jerry P. Burkes. Mr. Wally provided information and assistance.

Directors of WES during the work and the publication of this report were COL J. L. Cannon, CE, COL N. P. Conover, CE, and COL T. C. Creel, CE. Technical Director was Mr. F. R. Brown.

CONTENTS

CONVERSION FACTORS, NON-SI TO METRIC (SI) UNITS OF MEASUREMENT

Non-SI units of measurement used in this report can be converted to metric (SI) units as follows:

Multiply	By	To Obtain
Fahrenheit degrees	5/9	Celsius degrees or Kelvins*
feet	0.3048	metres
inches	25.4	centimetres
pounds (force) per square inch	0.006894757	megapascals

* To obtain Celsius (C) temperature readings from Fahrenheit (F) readings, use the following formula: C = (5/9)(F - 32). To Obtain Kelvin (K) readings, use: K = (5/9)(F - 32) + 273.15.

EXAMINATION OF ERDA-10
GROUT SPECIMENS AT DIFFERENT AGES

PART I: INTRODUCTION

1. The long-term stability of portland cement based grout under different conditions is of interest because such grout is a prime candidate as a repository sealing material for isolating nuclear wastes underground. The ERDA-10 experimental borehole in New Mexico[1] was provided with four grout plugs in October 1977. Core drilled from grout in that hole and samples cast at the surface when the hole was filled have been stored in the Structures Laboratory (SL) of the U. S. Army Engineer Waterways Experiment Station (WES) under a variety of conditions since that time. Portions of these specimens have been subjected to physical tests[2] and petrographic examination at ages of 23 $\pm$ 8 days, approximately 1 year, and approximately 3 years age to evaluate the effects of differences in composition, storage environment, and temperature on the grout samples with the passage of time. The results of the first petrographic examination are given in Appendix A. The results of the 1- and 3-year petrographic examination and some of the physical tests are given below. Detailed results of the physical tests will be reported separately. It is expected that portions of these specimens will be tested and examined at intervals in the future.

2. All four grout mixtures used in ERDA-10 were proportioned and placed by the staff of the Artesia, NM, batching plant of the Dowell Division of the Dow Chemical Company for Fenix and Sisson, project managers for Sandia Laboratories. Plugs 1, 2, and 3 were made with salt water and contained similar amounts of Type C oil well cement, fly ash, palygorskite (attapulgite) clay, quartz sand, and other minor ingredients.[1,2] Plug 4 was similar but had a lower water to cementitious solids ratio and contained no salt or sand.[1,2] The mixture proportions are given in [1]. The specimens from plugs 1, 2, and 3 have been kept in salt water at storage temperatures of 23° or 38° C most of the time; initially

the higher temperature was 54^{o} C because it was believed that this was the downhole temperature. This temperature was lowered to 38^{o} C after about 18 months when it was learned that this was closer to the actual temperature in the hole. Some of the plug 1 core was also kept at the higher temperature in brine; other parts of it were received in closed plastic bags and stored in laboratory air; these represent essentially dry storage at room temperature. The plug 4 specimens made with fresh water have been kept at about 23^{o} C under fresh water or in plastic bags kept in laboratory air.

PART II: EXPERIMENTAL

3. The procedures described in Appendix A were generally followed for the subsequent two examinations with the following exceptions:

a. Most of the 3 plus year old grout samples were each examined as a sawed surface rather than a ground powder by X-ray diffraction.

b. While interior areas were usually used for X-ray diffraction examination, the surfaces of several 3 plus year old specimens were examined to determine their composition. This was an additional examination.

c. A sponge soaked in room temperature barium hydroxide solution was used instead of a beaker of hot barium hydroxide solution in a static nitrogen atmosphere for X-ray diffraction examination of grouts made with salt. This was done when it was found that the higher humidity caused by the hot solution caused salt to concentrate at the specimen surface.

d. Scanning electron microscope (SEM) samples were vacuum-dried at 50° to 60° C or at 65° C instead of freeze-dried. The usual drying procedure now used is 16 hr at 50° C for specimens not containing salt. It was found that development of salt crystals growing on the fracture surfaces of SEM samples was minimized by heating these samples at 65° C for 24 hr before they were coated; these samples were also taken nearer to the center of each specimen to minimize saturation since this problem is caused by failure of the drying procedure to remove all possible moisture. In addition, the dried samples were mounted on SEM sample stubs in a room kept at 49° C and 24 percent relative humidity and kept in a dessicator during transport of samples to minimize carbonation. This modified drying procedure did not affect the phase composition of the grouts made with salt water.

4. Specimens were inspected for the development of cracks during the 3 plus year work. Four specimens (two pieces of plug 1 core and plug 2 and 4 cylinders) were photographed to illustrate the cracking that was found.

PART III: RESULTS

23- ± 8-Day-Old ERDA-10 Grout

5. As indicated in Appendix A:

   a. The surface cylinders made from plugs 1, 2, and 3 and the plug 1 core were similar in composition. They were composed of large amounts of tetracalcium aluminate dichloride-10-hydrate ($C_3A(CaCl_2)H_{10}$)* and calcium hydroxide and of smaller amounts of ettringite and unhydrated cement (including calcium silicates). Calcium silicate hydrate was not recognizable by X-ray diffraction at this time.

   b. None of the plug 4 grout that was made without salt was examined at this time.

   c. The microstructure of the grouts made with salt as shown by SEM was appropriate for these combinations of materials at these ages. Due to the short time that had elapsed since mixing the grouts, the microstructure showed considerable void space.

   d. It appeared that the chloride compound ($C_3A(CaCl_2)H_{10}$) was forming at the expense of ettringite in these grouts.

Nominal 1-Year-Old ERDA-10 Grout

6. The samples were actually about 14 months old when they were examined. The samples that were examined are listed below:

   a. Plug 1 core that had been stored in salt water at about 54° C.

   b. Plug 1 core that had been kept in a plastic bag in laboratory air at about 23° C.

   c. Plug 3 cylinder that had been stored in salt water at about 23° C.

   d. Plug 4 cylinder that had been stored in fresh water at about 23° C.

7. The above four samples were examined by X-ray diffraction and by SEM. Since no early age sample of plug 4 had been examined by X-ray

---

* Abbreviations where C = CaO, A = Al_2O_3, H = H_2O, $\bar{S}$ = SO_3, $\bar{C}$ = CO_2.

diffraction during the original work (Appendix A), a sample of plug 4 that had been in methanol in a freezer since it was 28 days old was examined by X-ray diffraction to represent the early age condition. Experimentation in the laboratory has shown that this is an effective way to cause hydration of portland cement to cease. A portion of plug 1 core from box 2, core barrel 2, was examined for air content by CRD-C 42-81.[3]

8. The results of these examinations were:

a. The X-ray diffraction patterns of the plug 1 and plug 3 grout that had been stored in salt water showed more $C_3A(CaCl_2)H_{10}$ than at the earlier ages (Appendix A) and no ettringite. This verified the earlier indication (Appendix A) that $C_3A(CaCl_2)H_{10}$ formed at the expense of ettringite. There was somewhat less calcium hydroxide, essentially all of the cement that would hydrate had done so, and calcium silicate hydrate was now recognizable.

b. Since the X-ray patterns described above were similar, this indicated that the range in temperature between about 23° C to about 54° C did not affect the composition of these samples.

c. The plug 1 sample that had been stored dry was like the early age sample in composition. The lack of water had effectively prevented or slowed down hydration.

d. Comparison of X-ray diffraction patterns of plug 4 at an intended early age and at 14 months indicated they were similar. Both contained ettringite, a lesser amount of tetracalcium aluminate monosulfate-12-hydrate ($C_4A\bar{S}H_{12}$), calcium hydroxide, calcium silicate hydrate (CSH), and a little quartz. There seemed to be more CSH than in the plug 1 or 3 grouts. The composition of the plug 4 grout was considered normal; lack of significant change with age was normal since most of the hydration would have occurred by 28 days.

e. The microstructure of the plug 1 and 3 grouts as seen by SEM was denser than it had been at the early ages (Appendix A). The microstructure of the plug 4 grout was normal for this material. Void space seen in SEM micrographs of plug 1 and plug 3 grout seemed about equal to that seen in plug 4 grout SEM micrographs. Approximately 50 SEM micrographs were made and studied. None are included in this report since it seemed preferable to show more of them at a later age.

f. The micrometric data for the plug 1 core sample are shown in Table 1; these values are similar to those for other samples of this core as shown in Table 1 of Appendix A.

Nominal 3-Year-Old ERDA-10 Grout

9. The samples were about 38 months old when they were examined by X-ray diffraction and SEM. Storage at about 54° C had been reduced to about 38° C at ages of about 18 months when the lower temperature seemed preferable. This is not considered significant since the earlier work had shown that temperature did not produce important effects in these ranges. The following samples were examined:

- a. Plug 1 core and cylinder material, both stored in salt water at about 38° C as noted above.
- b. Plug 3 cylinder material stored in salt water at about 23° C.
- c. Plug 4 cylinder material stored in fresh water at about 23° C.

10. These were the plug 1 and plug 3 samples where it was found that longer drying at a higher temperature was needed to prevent the growth of curved salt crystals on fresh fracture surfaces.

11. Examination of the samples by X-ray diffraction showed the following:

- a. While the heating at 65° C to improve drying did not seriously affect the $C_3A(CaCl_2)H_{10}$, calcium hydroxide, or CSH in the plug 1 and plug 3 grouts, the higher temperature did appear to cause some carbonation and to concentrate the salt (halite). The presence of some tetracalcium aluminate carbonate-11-hydrate ($C_4A\bar{C}H_{11}$) in the grout heated to 65° C was taken as a probable indication of this carbonation.
- b. The plug 1 and plug 3 grouts had similar compositions. These were $C_3A(CaCl_2)H_{10}$ and CSH with lesser amounts of calcium hydroxide, unhydrated cement (7.3 Å), quartz from the fly ash or sand or both, and probably some calcite; a little mullite from the fly ash was sometimes detectable.
- c. The amount of calcium hydroxide definitely decreased over the 3-year period. Since carbonation is not a major factor in the interior portions of these specimens, it may be assumed that the calcium hydroxide is combining with the fly ash to form CSH. There is less calcium hydroxide in plug 3 than in plug 1; this was also true at the earliest age of examination (not specified in Appendix A).

d. Examination of plug 1 grout core and plug 3 cylinder surfaces by X-ray diffraction showed that a great deal of carbonation had occurred at these surfaces during their storage in salt water or during their exposure to air during periodic testing or both; calcite was the major crystalline phase found; there was probably also some aragonite on these surfaces. The same pronounced carbonation was found on the surface of a plug 4 specimen kept in water; there was no indication of aragonite in this carbonated material but some vaterite may have been present.

e. The plug 4 interior grout contained calcium hydroxide, ettringite, and CSH along with a little probable calcite and vaterite, quartz, and unhydrated cement (7.3 Å). This composition had not changed much in 3 years; the probable presence of vaterite and calcite indicates a little carbonation has occurred.

f. As before, the difference in the grouts made with and without salt is the presence of $C_3A(CaCl_2)H_{10}$ and absence of ettringite with salt and vice versa.

12. Approximately 15 SEM micrographs were made of each sample for a total of about 60. Twelve of these were selected to illustrate the microstructure of these grouts at about 38-months age. Figures 1 through 8 show eight micrographs of the plug 1 and plug 3 grout at magnifications ranging from 200X to 5600X. They still show a porous microstructure at 38-months age. This is due to their high water to solids ratios of 0.64 to 0.74.[1,2] Overall, these grouts are denser than they were at 23 ± 8 days age (Appendix A) as would be expected. All of these eight micrographs represent grout dried 24 hr at 65° C to minimize salt crystal formation. Figure 4 shows grout dried 16 hr at 50° C and the curved salt crystals that resulted. Regardless of the drying procedure used, all eight of these micrographs show some evidence of salt crystals formed on drying the grout.

13. Figures 9 through 12 show four micrographs of the 38-month-old fresh water plug 4 grout at magnifications ranging from 500X to 20,000X. Comparison with Figures 1 through 8 show that the plug 4 grout has a denser structure. This is believed to be due to its lower water to solids ratio (0.49).[1,2] The microstructure of this plug 4 grout is more like that of the normal consistency paste with 30 percent fly ash shown in Photomicrographs 11 and 12 of Appendix A than the same age grouts made with salt.

14. The microstructures of the grouts as seen in Figures 1 through 12 are considered normal for these combinations of materials and age. The micrographs made and examined at the nominal 1-year age were much like those shown in Figures 1 through 12.

15. In general, calcium hydroxide, different morphologies of CSH, salt crystals, and an occasional sand grain can be recognized in the micrographs. While $C_3A(CaCl_2)H_{10}$ is known to be present from X-ray diffraction results in the grouts made with salt, it was not specifically recognized in these micrographs at any of the three ages that were examined.

16. No cracking of the grout specimens was noticed during handling and testing when they were about 1 year old. Some cracking was noticed at about the 2-year age. Close inspection of the grout specimens stored in brine at about 39 to 41 months of age showed that cracking was present in all of the specimens that remained. Some of this cracking was horizontal, some was vertical, some was diagonal, or was combinations of these types. There were some areas of crazing. Some of the cracks had healed and were marked by small ridges of precipitated material; others were open. All were narrow (i.e., <1 mm). Four photographs were taken to illustrate this cracking in plug 1 core, a plug 2 cylinder, and a plug 4 cylinder. These are shown in Figures 13 through 16. Inspection of the plug 1 grout core that had been kept in plastic bags in the laboratory for about 41 months showed that none of this core was cracked. For samples stored in brine, compressive strength values for pairs of 2-in.* cubes (approximate size) cut from cylinders at the 38-month age showed the following:

	Compressive Strength, psi
Plug 1 cylinder	4,400
Plug 2 cylinder	4,070
Plug 3 cylinder	3,320
Plug 4 cylinder	10,210

Since all but the plug 3 values represented a gain,(2) it is obvious the

* A table of factors for converting non-SI units of measurement to metric (SI) units is presented on page 3.

cracking (Figures 13, 14) has not seriously affected the strength of the grout. Plug 3 grout showed a decrease in strength from 3820 psi at 27 months to 3320 psi at 38 months. This may represent sampling variations rather than a real decrease in strength. During this time one of the plug 2 cylinders separated into two pieces when it was lifted; inspection of this broken surface did not suggest any problem other than progressive extension of an existing crack.

PART IV: DISCUSSION

17. Selected X-ray diffraction patterns were compared to determine what changes had taken place in the grout specimens during about 38 months of storage. Since all of the grouts made with salt (plugs 1, 2, 3) were similar at the ages they were examined, plug 1 core was used as an example of such grout. Comparison of X-ray diffraction patterns of it showed:

a. Plug 1 grout core.

(1) Ettringite was present at about 28-days age. It was no longer found at 1 year and was not found by 38 months.

(2) The amount of calcium hydroxide decreased with time.

(3) $C_3A(CaCl_2)H_{10}$ increased slightly to about 1 year and then remained about constant to approximately 38 months. This increase was associated with the decrease in ettringite.

(4) CSH was recognizable in X-ray diffraction patterns by 1 year and appeared to remain about constant to 38 months.

b. Plug 4 grout (made without salt).

(1) The amount of calcium hydroxide decreased with time.

(2) Other phases remained fairly constant.

18. Allowing for the differences in phase composition of the grouts made with salt water and the one made without salt, the changes in compositions have been gradual and normal for these materials.

19. The microstructure of the different grouts seemed normal and relatively unchanged with time except for the progress of hydration which tended to make a denser structure.

20. The specimens kept immersed in brine or fresh water at different tempe tures showed cracking; the remaining five pieces of plug 1 grout core showed less cracking than those grout specimens that had been cast at the surface of ERDA-10. There was some opportunity for drying of wet specimens when they were removed from storage for periodic testing or possibly if water levels fell during storage. In addition, there was storage in brine at about 54^{o} C of some specimens for about 18 months

followed by a reduction in temperature to about 38° C after that time. Since there was no cracking of plug 1 grout core kept dry at ambient laboratory temperature and there was cracking when there was opportunity for some drying or temperature change, the evidence suggests the cracking was due to the response of high cement content paste specimens to changes in the storage environment. The fact that cracking was common to brine and to fresh water indicates it was not a selective chemical reaction. Therefore, the cracking is considered normal for such specimens under the environmental changes that occurred and does not mean such cracking should be expected in the grout in the borehole. There the surrounding rock would moderate initial temperature rise and inhibit unrestrained expansion so that temperature and humidity should be essentially constant.

21. Scrapings from specimen surfaces were examined by X-ray diffraction. Those from the grouts made with salt and stored in salt water were highly carbonated. Scrapings from the plug 4 grout made without salt and stored in fresh water also showed much carbonation. The interiors of these specimens were not nearly so carbonated; this indicated that this carbonation was a surface condition due to the environment. No overall detrimental effects of this carbonation were recognized.

PART V: CONCLUSIONS

22. Study of portland-cement based grouts made with salt water and stored in salt water and of a similar grout made with fresh water and stored in fresh water at temperatures between about 23° C to 54° C over a period of 38 months showed:

a. Salt water grouts form tetracalcium aluminate dichloride-10-hydrate ($C_3A(CaCl_2)H_{10}$) at the expense of ettringite during hydration.

b. The amount of calcium hydroxide in both types of grout decreased with time, presumably due to its combination with fly ash in the mixture to form calcium silicate hydrate.

c. While the microstructure of the grouts tended to be open due to the fairly high water to solids ratios as mixed, it did become denser with time.

d. Phase composition and microstructure were considered normal for these mixtures and were generally unaffected by the conditions of storage.

e. Carbonation of the grouts made with salt water and stored in salt water was pronounced at specimen surfaces but not in their interiors. This is an effect of storage environment on the specimens.

f. The cracks that were observed in many specimens were considered normal for these materials under the storage and testing conditions. Since the storage and treatment of these specimens is not a simulation of conditions in a borehole, it is not believed that similar cracking would take place in this grout in such use.

g. Available data indicate the properties of the specimens are satisfactory for their intended use.

REFERENCES

1. Gulick, C. W., Jr., "Borehole Plugging Program, Plugging of ERDA No. 10 Drill Hole," Sandia Laboratories Report SAND79-0789, Jun 1979, Albuquerque, N. Mex.

2. Gulick, C. W., Jr., Boa, J. A., Jr., Walley, D. M., and Buck, A. D., "Borehole Plugging Materials Development Program Report 2," Sandia Laboratories Report SAND79-1514, Feb 1980, Albuquerque, N. Mex.

3. U. S. Army Engineer Waterways Experiment Station, CE, "Handbook for Concrete and Cement," with quarterly supplements, Vicksburg, Miss., Aug 1949.

4. Diamond, S., "Cement Paste Structure - An Overview at Several Levels," in Hydraulic Cement Pastes: Their Structure and Properties. Proceedings of a conference held at University of Sheffield, 8-9 Apr 1976, Cement and Concrete Association, Great Britain.

Table 1

Micrometric Data for Plug 1

Grout Core* from ERDA-10

Constituents	Amount, %**
Entrapped air	2.2
Cement paste	95.9
Sand	1.9
Total	100.0

* Box 2, core barrel 2.

** Done in accordance with CRD-C 42-81, Reference 3.

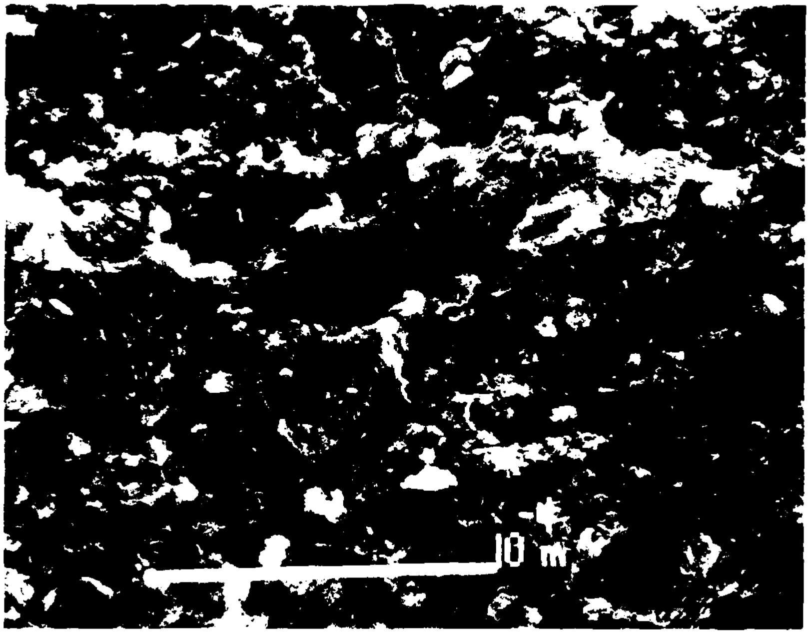


Figure 1. Micrograph 123080-30 (X500) of 38-month-old plug 1 grout. Typical microstructure showing considerable void space. The bar is 100 µm long

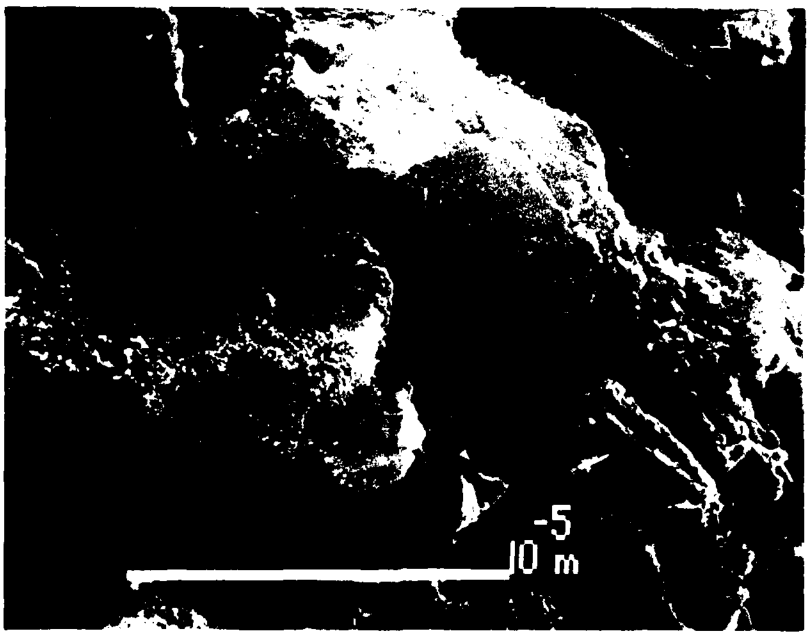


Figure 2. Micrograph 123080-1 (X5600). Different area of above sample. Massive calcium hydroxide with dried salt on surfaces. The bar is 10 µm long

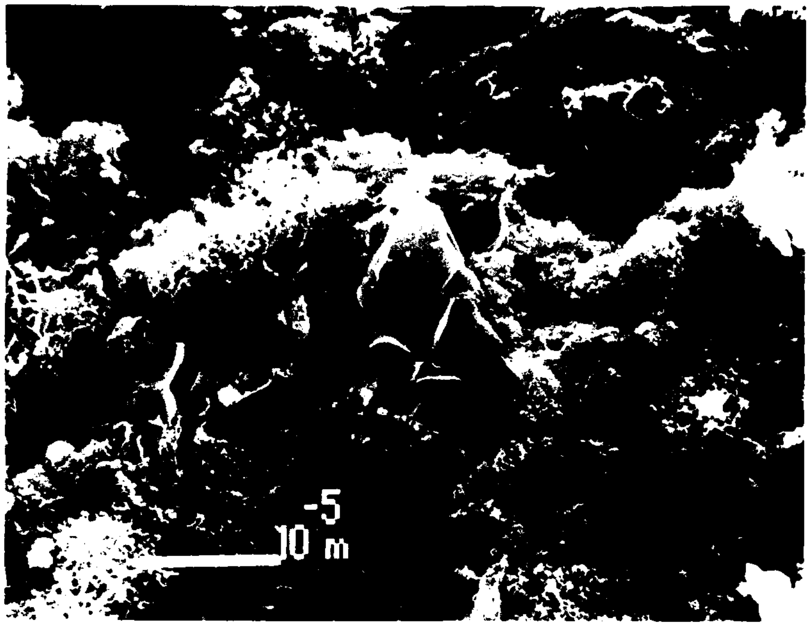


Figure 3. Micrograph 123080-7 (X2000) of 38-month-old plug 1 grout core. Typical porous microstructure showing CSH, calcium hydroxide, and dried salt. The bar is 10 μm long

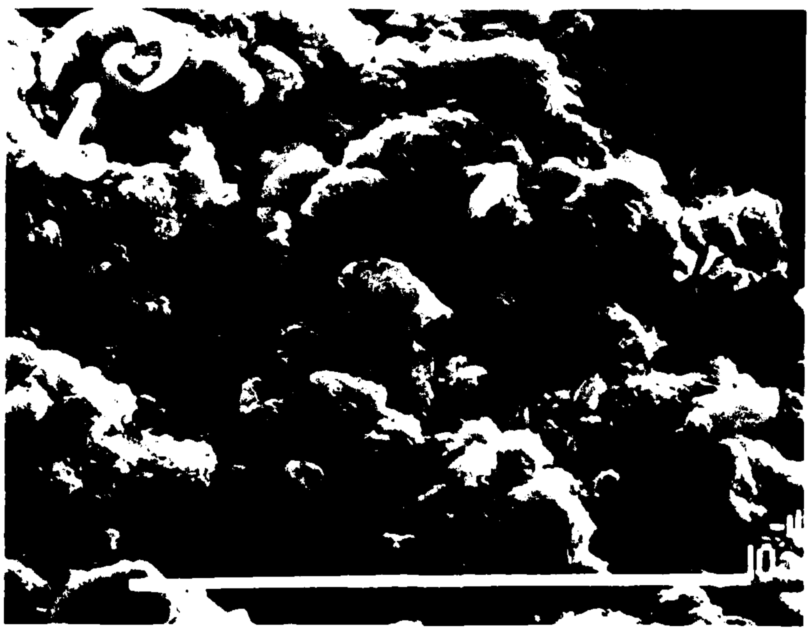


Figure 4. Micrograph 122380-36 (X900) of 38-month-old plug 1 grout core. The curved salt crystals indicate inadequate drying. The bar is 100 μm long

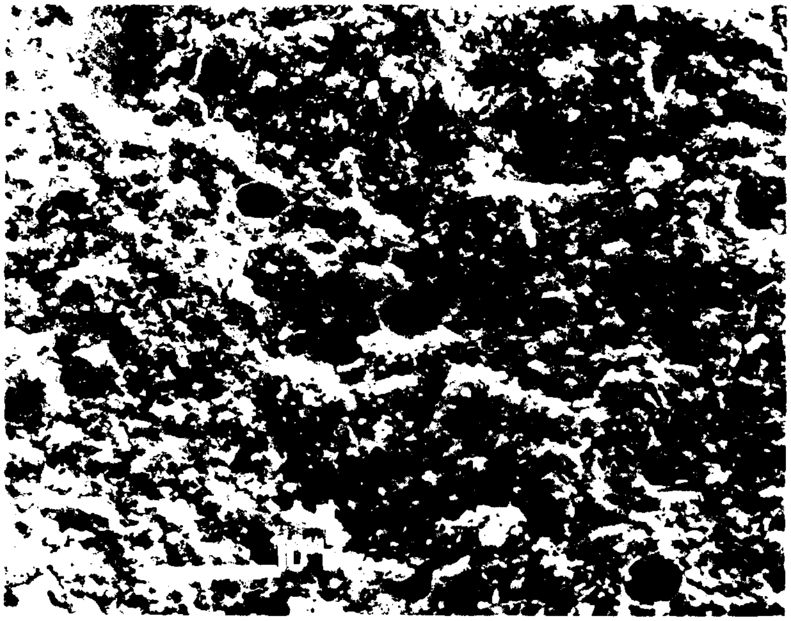


Figure 5. Micrograph 123080-36 (X200) of 38-month-old plug 3 grout. Typical porous microstructure. The bar is 100 μm long

Figure 6. Micrograph 123080-46 (X1000) of another area of Figure 5. The upper left area is probably a sand grain. The bar is 10 μm long

Figure 7. Micrograph 123080-38 (X2000). Another area of Figure 5. Some of the fine material on surfaces is probably dried salt. The bar is 10 μm long

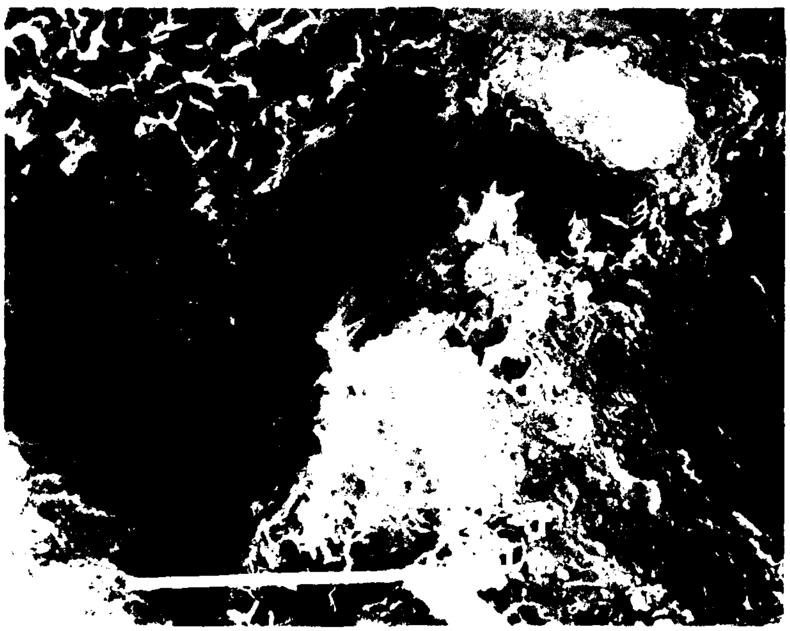


Figure 8. Micrograph 123080-41 (X5200). Higher magnification of center of Figure 6. Much of area appears to be reticulated Type II CSH.[4] The bar is 10 μm long

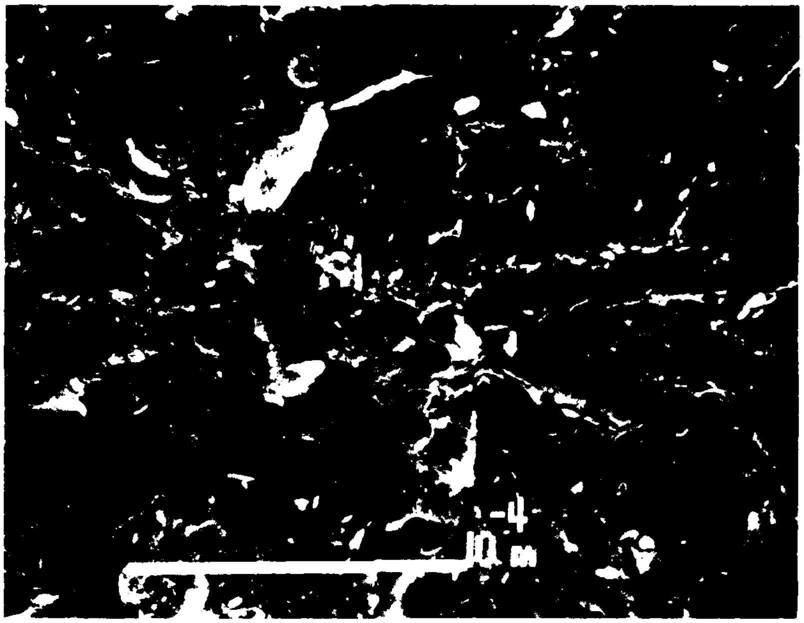


Figure 9. Micrograph 122380-6 (X500) of 38-month-old plug 4 grout made with fresh water. Denser than the grouts made with salt and more water. The bar is 100 μm long. Several fly ash spheres are evident

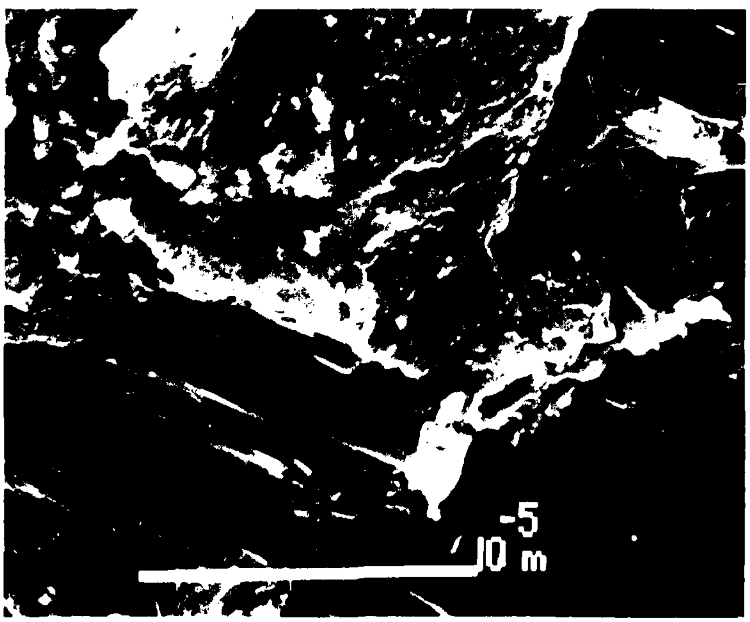


Figure 10. Micrograph 122380-3 (X5000). Higher magnification of central area of Figure 9. Massive calcium hydroxide and CSH. The bar is 10 μm long

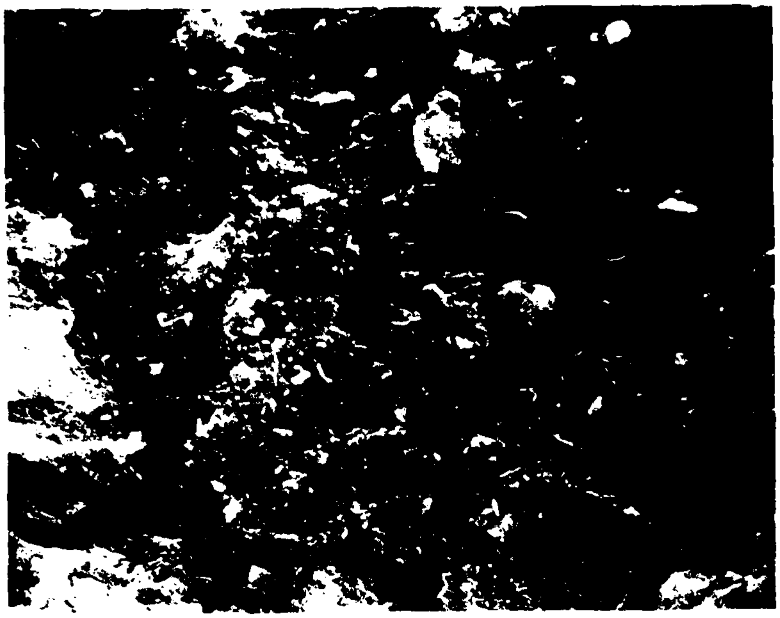


Figure 11. Micrograph 122380-12 (X1800) of 38-month-old plug 4 grout made with fresh water. Fairly dense microstructure

Figure 12. Micrograph 122380-8 (X20,000). Higher magnification of void in Figure 11. Void is partially filled with ettringite crystals. The bar is 1 μm long

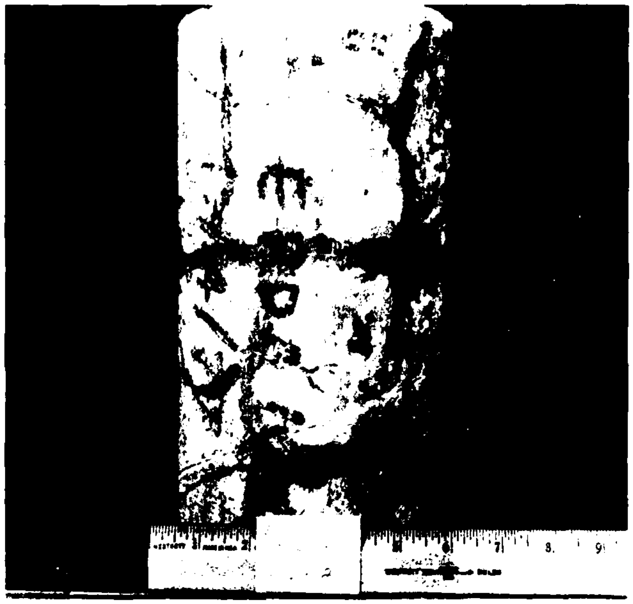


Figure 13. Thirty-nine-month-old plug 2 salt water grout cylinder partially dried by evaporation to accent cracking (damp areas)

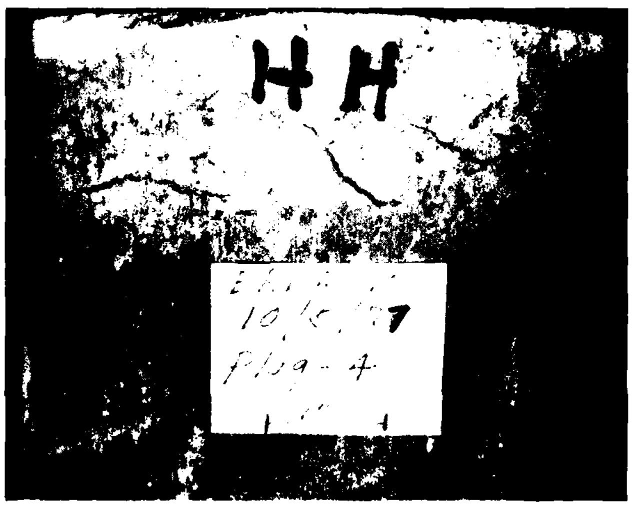


Figure 14. Thirty-nine-month-old plug 4 fresh water grout showing cracking near end of cylinder

Figure 15. Plug 1 3-in.-diameter grout core after about 41 months in brine at 100° F. Several filled cracks are evident; these include vertical, horizontal, and diagonal cracks

Figure 16. Plug 1 4-1/4-in.-diameter grout core after about 41 months in brine at 100° F. There is a vertical filled crack in this piece; it runs between the B in "CB" and the 3

APPENDIX A: PETROGRAPHIC REPORT

Corps of Engineers, USAE Waterways Experiment Station		Concrete Laboratory P. O. Box 631 Vicksburg, Mississippi
Project Examination of Grout Samples for Project ERDA-10		Date 4 January 1978 ADB

Background

1. The borehole known as ERDA-10, located in Eddy County, New Mexico, was filled with portland cement base grout in October 1977. Forty-eight hours later a portion of Plug 1 was removed as 4-in.-diameter core. Samples of this core, of control cylinders cast when the hole was filled, and of recirculated return grout from Plug 3 were received in the Concrete Laboratory (CL) on 17 October 1977. The 16-day-old specimens were examined at this time and at 28- to 31-day ages to answer the following two questions:

a. The hole was full of drilling mud before grout was introduced. Did the grout uniformly displace this mud upward or was there detectable contamination of the grout by the drilling mud?

b. It was anticipated that temperatures and pressures at or near the bottom of the 4431-ft-deep hole would be about 128° F (53° C) and 2000 psi (14 MPa). Did either or both of these conditions have any detectable effect on the hydration products in the grout?

Samples

2. Samples of the materials used in the grout were received shortly after 17 October 1977. All of the samples that were examined are identified below:

	Received at 16-days age. Examined at Age, Days
Plug 1 samples	
Batch 1 control cylinder	16; 28
Batch 2 control cylinder	16; 28
Cores from 3556- to 3595-, from 3595- to 3623-, and from 3623- to 3673-ft depths	16
Core from 3623- to 3673-ft depths from	
Barrel 3 Box 8	28
Barrel 3 Box 10	28
Plug 2 samples	
Control cylinder	28
Plug 3 samples	
Control cylinder	28
Recirculated return cylinder 1	29
Recirculated return cylinder 3	29
Recirculated return cylinder 5	29
Recirculated return cylinder 6	31

WES FORM No. 1115
Rev Feb 1970

Material	Description or Source
Type "C" cement	Texas
Fly ash	Texas
Salt Gel	Mixture of palygorskite * clay, sodium chloride, and water

3. Although there were no core samples from Plugs 2 or 3 the cylinders of recirculated return material did represent grout from Plug 3. Cylinder 6 of that material consisted of about 3 in. of solid material in the bottom of the cylinder and 9 in. of salty water.

Test procedure

4. The hydrated grout samples were examined by X-ray diffraction (XRD) and by scanning electron microscope (SEM). The air contents of several of these samples were determined by CRD-C 42.[1] The cement, fly ash, and dry palygorskite clay like that used in the salt gel were examined by X-ray diffraction.

5. All of the X-ray diffraction patterns were made with an X-ray diffractometer using nickel-filtered copper radiation.

6. The hydrated grout samples were ground but not sieved, and were mounted on the X-ray diffractometer as tightly-packed powders in a static nitrogen atmosphere saturated with hot barium hydroxide solution. The purpose of the nitrogen and the barium hydroxide is to prevent carbonation and dehydration of the samples.

7. All of the hydrated grout X-ray patterns contained material characterized by a spacing of 7.84 Å.** One of the control samples was exposed to dry ice in a moist atmosphere and then X-rayed to see if this treatment had any effect on the position of this peak. A small sample of the cement was mixed with water, allowed to hydrate for 15 days, and then examined by X-ray diffraction to determine whether the 7.84-Å peak would be absent in the absence of chloride.

8. The unhydrated cement was X-rayed as a tightly-packed powder in a static nitrogen atmosphere. The fly ash and palygorskite clay were X-rayed as tightly-packed powders in air. A portion of the cement was examined as a grain immersion mount with a polarizing microscope to determine if it were contaminated.

9. Five percent of the palygorskite clay by weight was blended with a ground sample of the Batch 2 control sample of grout from Plug 1 and this

---

* The term palygorskite is preferred to attapulgite for this clay.
** 0.784 nanometres.

mixture was X-rayed. The intent was to determine the approximate amount of salt gel or drilling mud that would have to be in the grout to be detected by X-ray diffraction.

10. The sawed and ground surfaces of several specimens of grout were examined with a stereomicroscope to see whether drilling mud or other foreign material was present.

11. Small portions of the grout samples were freeze-dried. A fresh fracture surface was then made on the dried material. The new surface was coated with about 50 Å of carbon and about 150 Å of an 80 percent gold-20 percent palladium alloy. These coated surfaces were then examined by SEM and photographs were made of selected areas at different magnifications.

Results

12. The X-ray data for the grout samples may be summarized as follows:

a. There was no salt gel or drilling mud detected in any of the core samples or in the recirculated return samples. Since the 5 percent palygorskite clay that was added to one grout sample was detected by X-ray examination, if there were palygorskite contamination, it was less than 5 percent.

b. All of the grout samples were similar. There were no detected and consistent differences between the surface control samples and the core or the recirculated return samples. This indicates that neither the combined nor the individual effects of elevated temperature and increased pressure on the hydration of the Plug 1 core and the Plug 3 recirculated return samples were significant.

c. There were no significant changes in the grout samples between the 16- and the 28- to 31-day ages.

d. The grout samples were characterized by the presence of small amounts of ettringite, large amounts of calcium hydroxide, substantial amounts of 7.84-Å material, and peaks in the diffraction pattern due to residual unhydrated portland cement. It is believed that the 7.84-Å material is the beta form of calcium monochloroaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$). Although this is not a normal hydration product of portland cement, it is a reasonable reaction product when chloride is present; both NaCl and $CaCl_2$ were added to the grout mixtures. In many of the X-ray patterns there appeared to be an unresolved peak on the low angle shoulder of the 7.84-Å peak; it is likely that this represented the presence of the alpha form of the chloroaluminate. The identification of the 7.84-Å peak as a hydrated calcium chloroaluminate was supported when this peak was missing in the X-ray pattern of the hydrated cement with no added chloride. Calcium silicate hydrate was presumably present but cannot be readily detected in hydrated cementitious materials of the ages of these samples.

e. Halite (NaCl) ranged from not detected to abundant* in the grout samples by X-ray diffraction. Its presence is indicated in the following tabulation:

	Halite
Plug 1	
Batch 1 control cylinder	Present
Batch 2 control cylinder	Not detected
Core - 3 pieces	Not detected
Plug 2	
Control cylinder	Abundant
Plug 3	
Control cylinder	Present
Recirculated return cylinder 1	Not detected
Recirculated return cylinder 3	Not detected
Recirculated return cylinder 5	Not detected
Recirculated return cylinder 6	Abundant

13. The halite was always detectable on sawed surfaces by taste. Its presence was also usually indicated on sawed surfaces by a white efflorescence that developed over a period of days. Other observations include:

a. Occasional small pieces of reddish rock (probably anhydrite) were found on sawed surfaces of the cores, but there was no significant amount of contamination by wall rock from the hole.

b. Examination of the core samples and of their sawed surfaces visually and with a stereomicroscope did not show any detectable contamination by drilling mud.

c. The high insoluble residue (4.35 percent) found by chemical analysis of the cement indicated that it was contaminated. Examination of an immersion mount of cement with a polarizing microscope confirmed this conclusion and showed that the contaminant was fly ash.

14. Fly ash was not detected in the cement by X-ray diffraction and its detection would not be expected at the level shown chemically. X-ray examination did show that this was a high alite, low belite cement without any detectable tricalcium aluminate; the sulfate was present as anhydrite; a calcium aluminoferrite was present.

15. The crystalline phases in the fly ash that were detected by X-ray were quartz, mullite, calcium oxide, and hematite. Those in the clay material used in the salt gel were mainly palygorskite clay with small amounts of 14-Å clay, clay-mica, and quartz.

---

* Later work indicates that it tends to dissolve in the high humidity of hot barium hydroxide. It then may reprecipitate so distribution is uneven.

16. Air void and other micrometric data are shown in Table A1 for seven samples of grout. The range of 1.6 to 3.3 percent air for the two control samples and the range of 2.0 to 2.6 percent air for the three core samples, all from Plug 1, indicate no significant changes due to pumping or to environment in the hole. The 5.6 percent air in the Plug 3 control cylinder indicates more air in this mixture; the additional pumping of the recirculated return cylinder 3 sample apparently caused its air content to increase to 8.0 percent.

17. The SEM photomicrographs did not show substantial differences between the control and plug samples at any age examined. This is in agreement with the other data. Photomicrographs 1a, 2a, and 4a show the typical appearance of the grout at 16- and 28-day ages. Photomicrographs 2b, 3b, 4b, and 5b are more highly magnified views that show the porous nature of the grout. Photomicrographs 6a and 6b are of a 28-day-old Type I portland cement paste with 30 percent fly ash that was made to normal consistency; the lower water content of this sample results in a much denser structure than seen in the grout samples. Photomicrograph 1b shows typical salt crystal development in a void in a control specimen of grout. Photomicrograph 3a shows an unusual appearance that was attributed to moisture pickup by the salt and its subsequent deposition during sample preparation. Photomicrograph 5a shows well developed platy crystals that may be the calcium monochloroaluminate hydrate that was identified by X-ray diffraction.

Discussion

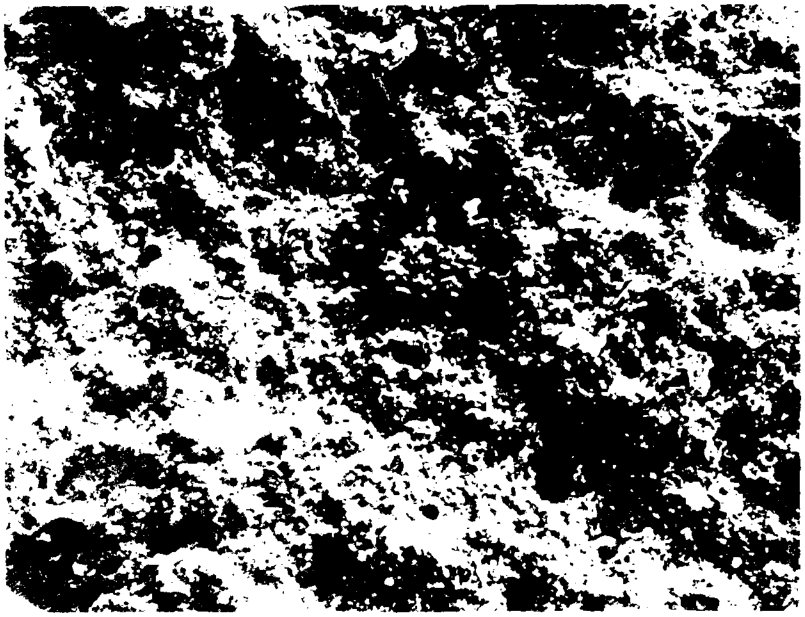
18. The work that was done has shown that there was no appreciable contamination of the Plug 1 or Plug 3 grout by the drilling mud that it displaced as the hole was filled. The similarity of the grout from the ERDA-10 hole and of the control specimens indicated that neither the temperature nor the pressure in the hole had any appreciable effects on the hydration products that were formed. However, the presence of chloride did cause the formation of calcium monochloroaluminate hydrate in all of the samples. The presence of this compound probably caused the amount of ettringite formed to be lower than usual since some of its aluminum went into the chloride bearing compound. This is not considered significant since neither compound contributes to the strength of the grout. Halite was present in many samples.

Table A1

Micrometric Data* for Seven Grout Samples, Project ERDA-10

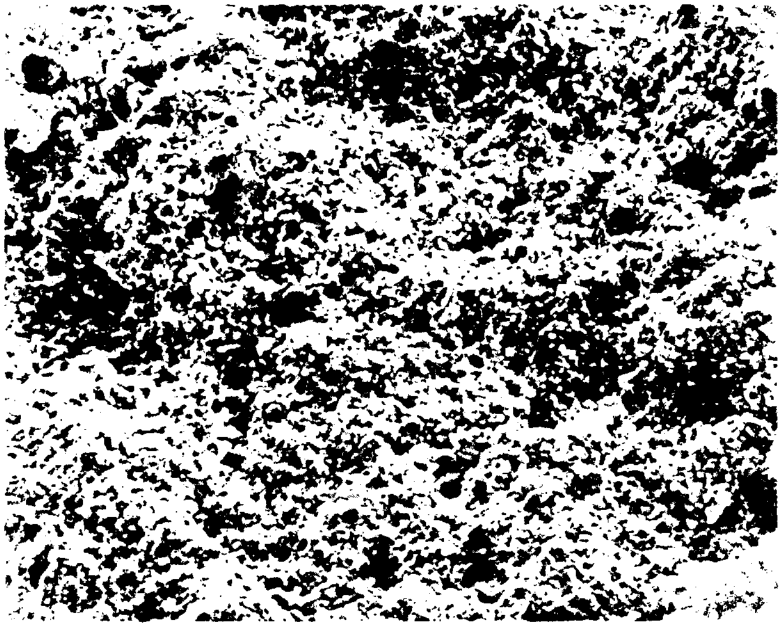
	Plug 1 Samples					Plug 3 Samples	
Micrometric Data, %	Control Cylinder 1	Control Cylinder 2	Core, in 3556- to 3595-ft Interval	Core, in 3595- to 3623-ft Interval	Core, in 3623- to 3673-ft Interval	Control Cylinder	Recirculated Return Cylinder 3
Entrapped air	3.3	1.6	2.4	2.6	2.0	5.6	8.0
Quartz	2.8	2.6	3.6	3.1	4.0	2.1	3.0
Paste	93.9	95.8	94.0	94.3	94.0	92.3	89.0
Total	100.0	100.0	100.0	100.0	100.0	100.0	100.0

* CRD-C 42-71, Reference 3.

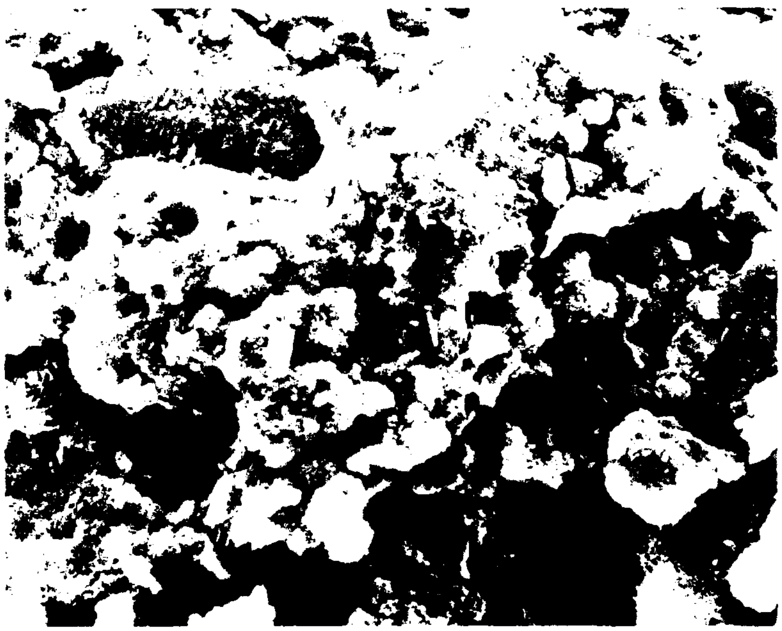


Photomicrograph 1a. Twenty-eight-day-old grout sample from Batch 1 control for Plug 1, X88. Typical of both batches and also of 16-day-old controls

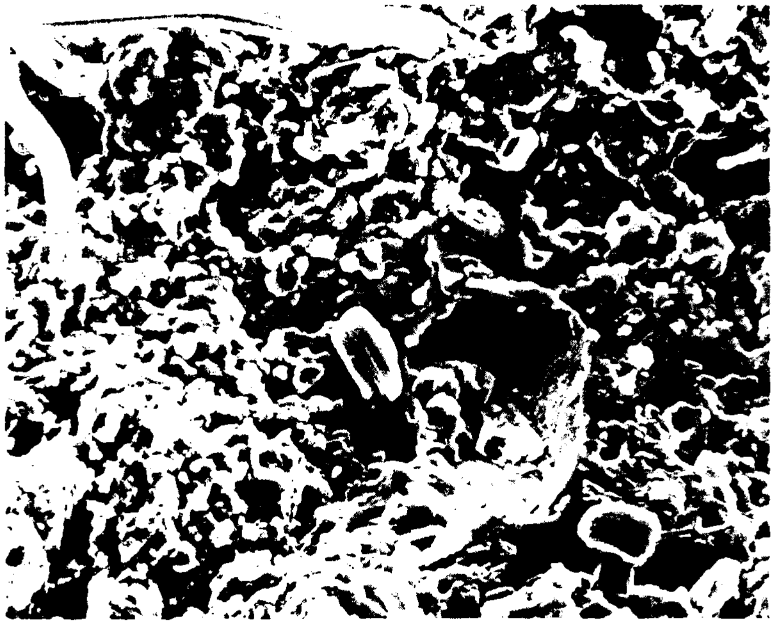
Photomicrograph 1b. Enlargement of halite crystals in void in center part of 1a, X440



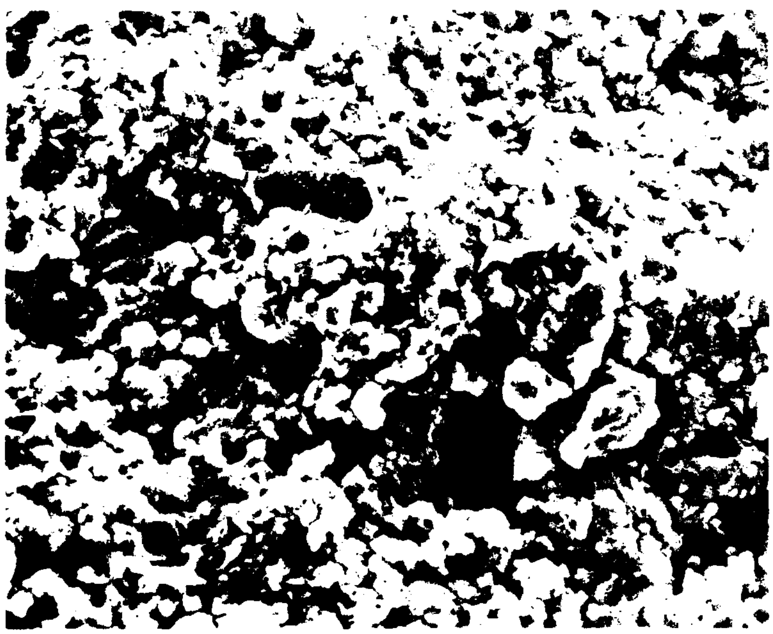
Photomicrograph 2a. Twenty-eight-day-old grout sample, core from Plug 1, Barrel 3, Box 8, X170. Similar in appearance to the control in 1a



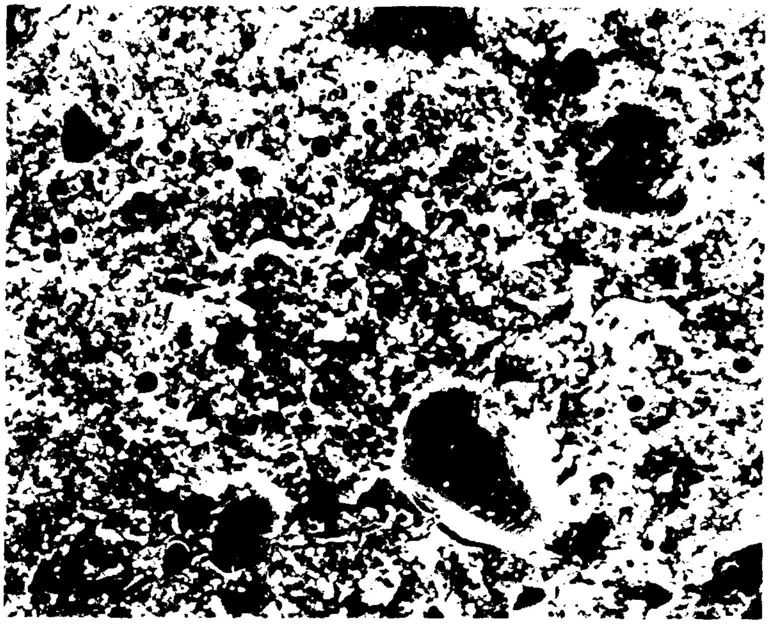
Photomicrograph 2b. Same as above, X1700. Note the porous appearance. This appears to be calcium silicate hydrate coating residual cement grains. The material at the right center is probably calcium hydroxide



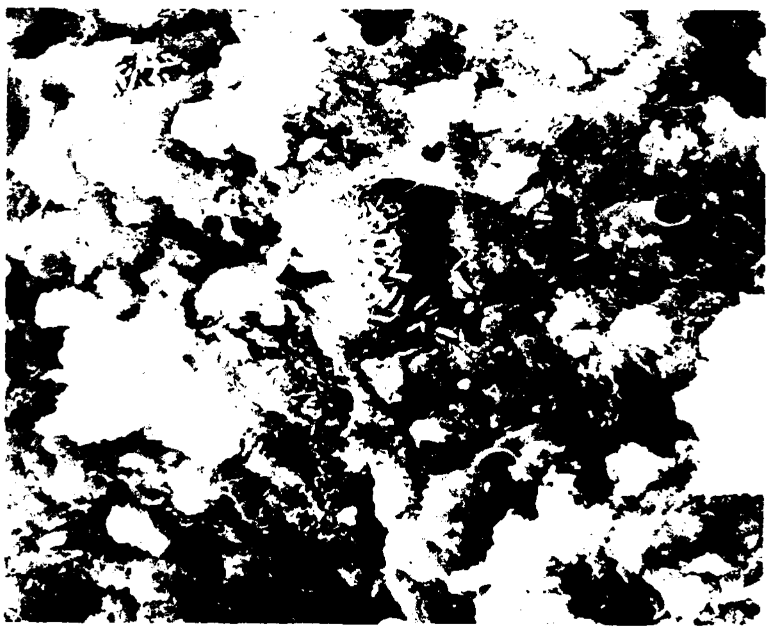
Photomicrograph 3a. Twenty-eight-day-old grout sample from Plug 1 core, Barrel 1, Box 10, X920. This is atypical and is believed due to whiskers of halite that developed during sample preparation



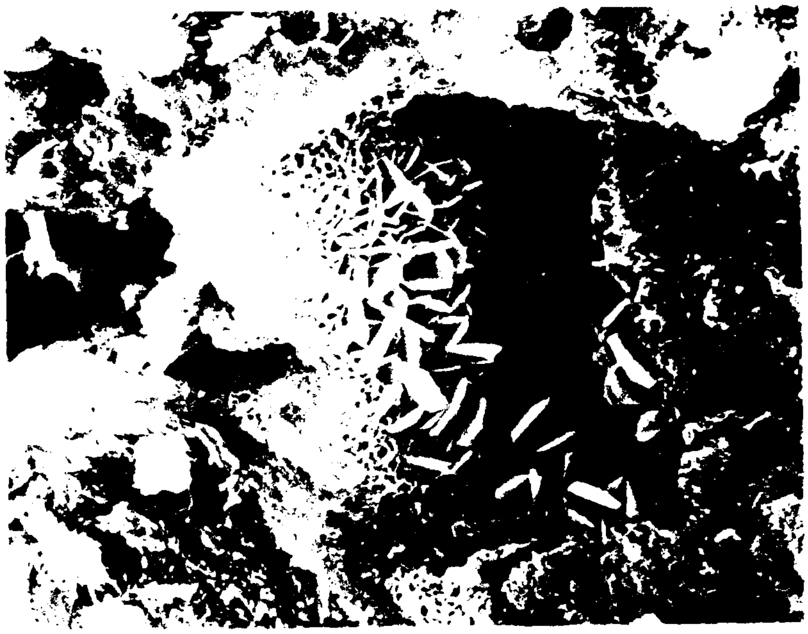
Photomicrograph 3b. Same as above but Barrel 3, Box 8, X850. Typical appearance of this material at 16- and 28-day ages. This is an intermediate magnification to those in 2a and 2b



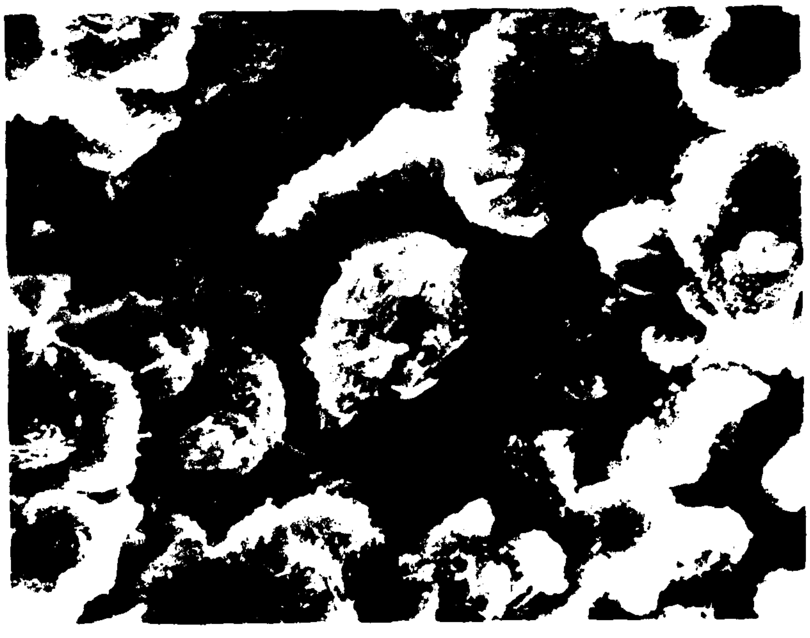
Photomicrograph 4a. Twenty-eight-day-old grout from control cylinder for Plug 3, X190. Several air voids are evident



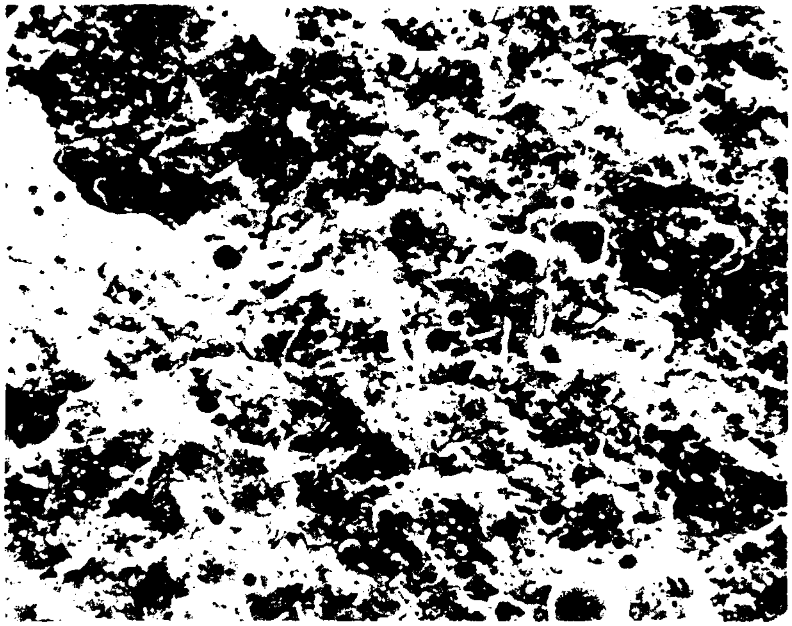
Photomicrograph 4b. An area of 4a at X1900. Note the porous appearance



Photomicrograph 5a. Same as 4b at X4750. The tabular crystals may be calcium monochloroaluminate hydrate



Photomicrograph 5b. Thirty-one-day-old grout sample from recirculated return cylinder 6, X1920



Photomicrograph 6a. Twenty-eight-day-old normal consistency Type I portland cement paste with 30 percent fly ash, X200. Compare this dense paste with the porous appearance of the grout in 1a, 2a, and 4a

Photomicrograph 6b. A portion of 6a at X2000. Compare with 2b, 4b, and 5b

In accordance with letter from DAEN-RDC, DAEN-ASI dated 22 July 1977, Subject: Facsimile Catalog Cards for Laboratory Technical Publications, a facsimile catalog card in Library of Congress MARC format is reproduced below.

Buck, Alan D.
  Examination of ERDA-10 grout specimens at different ages : final report / by Alan D. Buck, Jerry P. Burkes, Jay E. Rhoderick (Structures Laboratory, U.S. Army Engineer Waterways Experiment Station). -- Vicksburg, Miss. : The Station ; Springfield, Va. : available from NTIS, [1981].
  25, 13 p. : ill. ; 27 cm. -- (Miscellaneous paper / U.S. Army Engineer Waterways Experiment Station : SL-81-20)
  Cover title.
  "August 1981."
  "Prepared for Sandia National Laboratories and Office of Nuclear Waste Isolation, Battelle Memorial Institute."
  Bibliography: p. 16.

  1. Boring. 2. Grout (Mortar). 3. Electron microscopy. 4. Radioactive wastes. 5. X-rays--Diffraction. I. Burkes, Jerry P. II. Rhoderick, Jay E. III. Sandia National Laboratories. IV. Battelle Memorial Institute. Office of

Buck, Alan D.
  Examination of ERDA-10 grout specimens : ... 1981.
(Card 2)

Nuclear Waste Isolation. V. U.S. Army Engineer Waterways Experiment Station. Structures Laboratory. VI. Title VII. Series: Miscellaneous paper (U.S. Army Engineer Waterways Experiment Station) ; SL-81-20.
TA7.W34m no.SL-81-20